PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C09D 175/16, C08G 18/67 — A1

(11) International Publication Number: WO 94/29398

(43) International Publication Date: 22 December 1994 (22.12.94)

(21) International Application Number: PCT/NL94/00113

(22) International Filing Date: 18 May 1994 (18.05.94)

(30) Priority Data:
9300564 3 June 1993 (03.06.93) BE

(71) Applicant *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: WESTERHOF, Henk [NL/NL]; Vereningingstraat 79, NL-8012 BB Zwolle (NL). WEHMAN, Erik [NL/NL]; Kokmeeuw 19, NL-3831 HH Leusden (NL). RIETBERG, Johan [NL/NL]; Penningkruidweg 36, NL-8042 NR Zwolle (NL).

(74) Agent: SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: RADIATION-CURABLE AQUEOUS URETHANE (METH)ACRYLATE DISPERSIONS BASED ON ISOCYANATES, (METH)ACRYLATE MONOMERS AND AN INTERNAL EMULSIFIER

(57) Abstract

The invention relates to radiation-curable aqueous urethane (meth)acrylate dispersions based on diisocyanates, (meth)acrylate monomers and an internal emulsifier. The internal emulsifier is radiation curable and comprises maleic anhydride units and alkylene oxide units. The dispersion results in coatings being scratch resistant and resistant to chemical substances.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

RADIATION-CURABLE AQUEOUS URETHANE (METH)ACRYLATE DISPERSIONS BASED ON ISOCYANATES, (METH)ACRYLATE MONOMERS AND AN INTERNAL EMULSIFIER

The invention relates to radiation-curable aqueous urethane (meth)acrylate dispersions based on isocyanates, (meth)acrylate monomers and an internal emulsifier.

Such dispersions are described by Oldring in 'Chemistry and Technology of UV and EB formulation for coatings, inks and paints' (Volume 2, 1991, pp. 185-206).

A drawback of these dispersions is that they result in coatings having an insufficient scratch resistance and having an unsufficient resistance to chemical substances after curing.

The object of the invention is to provide a radiation-curable urethane(meth)acrylate dispersion which results in coatings having good scratch resistance, being resistant to chemical substances and having also other desired properties such as for example a good flow, sandability, gloss and emulsion stability.

The invention is characterised in that the internal emulsifier comprises (1-4) units of maleic anhydride (MA).

Preferably the emulsifier comprises (1-2) units of maleic anhydride. This emulsifier is radiation-curable.

Preferably, the emulsifier also comprises alkylene oxide units.

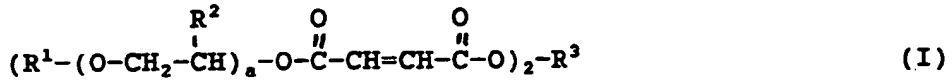
Preferably the alkylene oxide is ethylene oxide. Other suitable alkylene oxides include, for example, propylene oxide and ethylene oxide/propylene oxide block copolymers.

The use of the emulsifier according to the

invention ensures that the acrylate groups react with one another during the radiation curing of the film while the double bond (resulting from MA) in the emulsifier system also takes part in the reaction. As a result, a hard coating with a good resistance to chemical substances and good scratch resistance is obtained after curing. Moreover this coating can be very well sanded. Other desired properties, such as for example a good hardness, a good flow, and a good gloss are also obtained.

The incorporation of the reactive emulsifier according to the invention also results in an improved emulsion stability.

According to a preferred embodiment of the present invention the emulsifier is represented by formula (I):



(I)

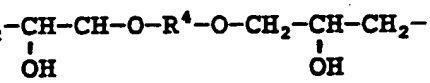
in which:

a = 5-50,

R^1 = (C_1-C_4) alkyl,

R^2 = H or CH_3,

and



in which

R^4 = (C_6-C_{75}) aromatic compound,
(C_6-C_{75}) cycloalkyl or
(C_6-C_{75}) alkyl and

the aromatic compound, cycloalkyl and alkyl are based on diglycidyl compounds.

The preparation of the emulsifier system according to formula (I) can take place by carrying out, in a first step, a reaction between an alkoxypolyalkylene glycol and maleic anhydride, at temperatures between 100°C

and 200°C, preferably between 110°C and 130°C, for a period of preferably 1-3 hours. In a second step, the product obtained in the first step is then reacted with a diglycidyl ether, for 1-3 hours, at temperatures of between 100°C and 200°C, preferably between 140°C and 150°C.

Suitable alkoxypolyalkylene glycols include, for example, methoxypolyethylene glycol (MPEG), butoxy-polyethylene glycol and alkoxy copolymers of ethylene glycol and propylene glycol.

Preferably use is made of MPEG. The molar weight is preferably between 500 and 1000.

Suitable diglycidyl ethers include for example the diglycidyl ether of bisphenol A, diglycidyl ether of butane diol, diglycidyl ether of neopentyl glycol and the diglycidyl ether of cyclohexane dimethanol.

Preferably use is made of the diglycidyl ether of bisphenol A.

The molar ratio alkoxypolyalkylene glycol to acid anhydride is usually between 1:0.9 and 1:1.1 and is preferably between 1:1.0 and 1:1.05. The molar ratio of the reaction product of alkoxypolyalkylene glycol and anhydride to diglycidyl ether is usually between 1:0.45 and 1:0.6 and is preferably between 1:0.50 and 1:0.55.

The reactions can be carried out either solvent-free or in the presence of solvents such as, for example, toluene, xylene and N-methylpyrrolidone. The reactions are preferably carried out in the absence of solvents.

The two reactions can be carried out either with or without catalysts. Suitable catalysts include, for example, tertiary amines such as for example dimethylbenzylamine and triethylamine, phosphines, phosphonium compounds and tetraalkylammonium halogenides such as for example tetramethylammonium bromide. The catalysts can be used in amounts of between, for example, 0.025 and 0.5 % by weight.

According to a preferred embodiment of the

present invention, in formula (I):

a = 15-20,

R^1 = methyl,

R^2 = H

and

R^3 = $-CH_2-\underset{OH}{CH}-CH_2-O-R^4-O-CH_2-\underset{OH}{CH}-CH_2-$

in which $R^4 = -(C_6H_4)-C_3H_6-(C_6H_4)-$

According to another preferred embodiment of the present invention the emulsifier is represented by formula (II):

$$R^5-(O-CH_2-\underset{R^6}{CH})_b-O-\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}-O-R^7 \qquad (II)$$

in which:

b = 5-50,

R^5 = (C_1-C_4) alkyl,

R^6 = H or CH_3,

R^7 = $-CH_2-\underset{OH}{CH}-\underset{OH}{CH}-R^8$

in which R^8 = H or (C_1-C_4) alkyl.

The preparation of the emulsifier system according to formula (II) can take place by carrying out, in a first step, a reaction between an alkoxypolyalkylene glycol and maleic anhydride, at temperatures between 100°C and 200°C, preferably between 110°C and 130°C, for 1-3 hours. The reaction product obtained then reacts, in a second step, with an epoxy alcohol, for 1-3 hours, at temperatures between 100°C and 200°C, preferably at temperatures between 130°C and 140°C.

The alkoxypolyalkylene glycol used is preferably methoxypolyethylene glycol (MPEG). The molar weight is preferably between 500 and 1000. Other suitable alkoxypolyalkylene glycols are for example

butoxypolyalkylene glycol and alkoxy copolymers of ethylene glycol and propylene glycol.

The epoxy alcohol used is preferably glycidol.

The molar ratio of alkoxypolyalkylene glycol to anhydride is usually between 1:0.9 and 1:1.1 and is preferably between 1:1.0 and 1:1.05. The molar ratio of the reaction product of alkoxypolyalkylene glycol and anhydride to epoxy alcohol is usually between 1:0.9 and 1:1.15 and is preferably between 1:1.0 and 1:1.1.

The two reactions can be carried out either with or without catalysts. Suitable catalysts include, for example, tertiary amines such as dimethylbenzylamine and triethylamine, phosphines, phosphonium compounds and tetraalkylammonium halogenides such as tetramethylammonium bromide. The catalysts can be used in amounts of between, for example, 0.025 and 0.5 wt.%.

The reactions can be carried out either solvent-free or in the presence of solvents such as for example toluene, xylene or N-methylpyrrolidone. The reactions are preferably carried out in the absence of a solvent.

According to a preferred embodiment of the present invention, in formula (II):

b = 15-20,

R^5 = methyl,

R^6 = H,

R^7 = $-CH_2-\underset{OH}{CH}-\underset{OH}{CH}-R^8$

in which

R^8 = H.

Urethane (meth)acrylate oligomers can for example be prepared via the reaction of diisocyanates, (meth)acrylate monomers containing hydroxyl groups and the emulsifier according to the present invention. To obtain certain desired properties diols and polyols may also be added in addition to said components.

The emulsifier precursor according to formula

(I) or (II), mixed with the desired diols or polyols, may react with isocyanates, for 1-3 hours, at temperatures between 50°C and 100°C, preferably between 75°C and 85°C. The product obtained in the first step may react in a second step with the (meth)acrylate monomer containing hydroxyl groups, for 3 to 5 hours, at a temperature between 50°C and 100°C, preferably between 75°C and 85°C.

The product obtained (having a temperature of, for example, 75°C-85°C) is then dispersed in water having a temperature of between, for example, 20°C and 50°C. During the dispersing any isocyanate groups still present may react with water or diamine, which results in chain growth.

The molar ratio of the total of hydroxyl groups from the acrylate monomers, diols, polyols and emulsifier to the isocyanate groups molar ratio is usually between 0.6 and 1.2 and is preferably between 0.95 and 1.

The reactions described may optionally be carried out in the presence of a solvent; it is however preferable to carry them out in the absence of solvents.

Suitable isocyanates may be both aromatic and aliphatic. Suitable aromatic diisocyanates include, for example, toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Suitable aliphatic diisocyanates include for example isophoron diisocyanate (IPDI), hexamethylene diisocyanate (HMDI) and oligomers of HMDI and hydrogenated MDI (H12-MDI). Aliphatic diisocyanates having aromatic rings such as, for example, tetramethylene xylene diisocyanate (TMXDI) and xylene diisocyanate (XDI) may also be used.

Preferably IPDI and TDI are used.

Suitable (meth)acrylate monomers containing hydroxyl groups include for example hydroxyethyl (meth)acrylate and hydroxypropyl acrylate.

Preferably hydroxyethyl acrylate is used.

Various polymers (having a molar weight of between approximately 500 and 4000) may be used as the

diol, provided that they have terminal OH groups. Suitable polymers include for example polypropylene glycol, linear polyesters, polycaprolactones, polycarbonates or polytetrahydrofurans. In addition to these polymeric diols use may be made of low-molecular weight polyols. Suitable diols include for example 1,4-butanediol and 1,6-hexanediol. Suitable polyols include for example trimethylolpropane, pentaerythritol, dipentaerithritol and dimethylolpropane.

The alkylene oxide content of the synthesized product is generally between 0.5 and 50.0 wt.%.

The preparation of aqueous urethane acrylate dispersions is described by Oldring in 'Chemistry and Technology of UV and EB formulation for coatings, inks and paints', (Vol. 2, 1991, pp. 73-79) the disclosure of which is incorporated herein by reference.

The radiation curing of the urethane (meth)acrylate dispersion preferably takes place by means of UV or EB curing. Both curing methods are described by S.J. Bett et al. in the article 'UV and EB Curing' in Jocca (1990 (11), pp. 446-452) the disclosure of which is incorporated herein by reference.

The dispersions according to the invention may be used in the preparation of coatings which can be applied to various substrates such as, for example metal, wood, textile, leather, plastic and paper. Other fields of application include for example the ink and adhesive industries.

The emulsifiers according to the invention, in particular the emulsifier according to formula (I), may also be used in combination with other radiation-curable systems such as, for example, dispersions based on epoxy acrylates and polyester acrylates.

The present invention is illustrated with the aid of the following, non-restrictive, examples.

Example I

Preparation of an emulsifier system according to formula (I)

714 parts by weight of methoxypolyethylene glycol (MPEG) and 98 parts by weight of maleic acid anhydride (MA) were heated to 120°C in a vessel provided with a stirrer, under nitrogen. After 3 hours at 120°C (at an acid number of 71 mg of KOH/g of resin) 188 parts by weight of diglycidyl ether of bisphenol (Epikote 828™) were added. After 2 hours at 145°C an acid number of < 5 was reached.

The reaction product had the following constants:
hydroxyl value: 58 mg of KOH/g of resin;
acid number: < 5 mg of KOH/g of resin.

Example II

Preparation of an emulsifier system according to formula (II)

804 parts by weight of methoxypolyethylene glycol (MPEG) and 111 parts by weight of maleic anhydride (MA) were heated to 120°C under nitrogen in a vessel provided with a stirrer. After 3 hours at 120°C (at an acid number of 71) 85 parts by weight of glycidol were added. After 2 hours at 135°C an acid number of < 5 was reached.

The reaction product had the following constants:
hydroxyl value: 120 mg of KOH/g
acid number: < 5 mg of KOH/g.

Example III

Preparation of an urethane acrylate dispersion

155 parts by weight of the emulsifier system according to Example I, 24 parts by weight of trimethylolpropane (TMP) and 153 parts by weight of isophoron diisocyanate were mixed and the mixture was

heated to 90°C. After 3 hours at 90°C, 68 parts of hydroxyethyl acrylate (HEA) were added dropwise to the mixture, which had an NCO content of 8.7%. After 5 hours' reaction at 90°C the NCO content was 1%. Then the product was pumped into a dispersing vessel, into which 600 parts by weight of demineralized water had been introduced. Chain growth subsequently took place. The dispersion was drained at an NCO content of 0%.

Example IV

Preparation of a urethane acrylate dispersion

134 parts by weight of the emulsifier system according to Example II, 21 parts by weight of trimethylolpropane (TMP) and 168 parts by weight of isophoron diisocyanate were mixed and the mixture was heated to 90°C. After 3 hours at 90°C 77 parts of hydroxyethyl acrylate (HEA) were added dropwise to the mixture, which had an NCO content of 9.8%. After 5 hours' reaction at 90°C the NCO content was 1%. Then the product was pumped to a dispersing vessel, into which 600 parts by weight of demineralized water had been introduced. Chain growth subsequently took place. The dispersion was drained at an NCO content of 0%.

Example V

UV curing

4% by weight solid substance of a 3.2 gram of 50% solution of 1-hydroxycyclohexylphenylketone (Irgacure 184™) in ethanol was added to 100 grams of the dispersion according to Example III. This dispersion was applied to a wooden panel with the aid of a 30-μm wire coater. This was then dried for 5 min. at 50°C to evaporate the water, after which crosslinking took place as a result of irradiation using a medium-pressure Hg lamp (dose 750 mJ/cm^2). Two layers were applied, the first of which was sanded with sandpaper after application.

The characteristics of the coating are summarized in Table 1.

TABLE 1

particle size:	80 nm
weight per unsaturation:	510
König hardness (1)	125
scratch resistance (2)	1
resistance to ethanol (3)	1
resistance to xylene (3)	0
resistance to coffee (3)	0

(1) determined by DIN 53157

(2) determined visually using a wire-brush:
0 = very good
1 = good
2 = satisfactory
3 = moderate
4 = poor

(3) determined according to DIN 68 861-1A:
0 = very good
1 = good
2 = satisfactory
3 = moderate
4 = poor

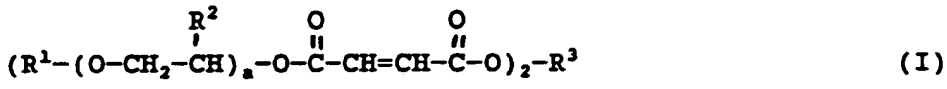
These examples show that the internal emulsifier according to the present invention results in a good scratch resistance and a good resistance to chemical substances of the radiation-cured coating.

C L A I M S

1. Radiation-curable aqueous urethane (meth)acrylate dispersion based on isocyanates, (meth)acrylate monomers and an internal emulsifier, characterised in that the internal emulsifier comprises (1-4) units of maleic anhydride.

2. Dispersion according to claim 1, characterised in that the emulsifier comprises alkylene oxide units.

3. Dispersion according to any one of claims 1-2, characterised in that the emulsifier is represented by formula (I):



(I)

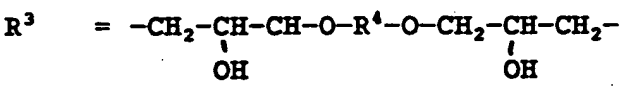
in which:

a = 5-50,

R^1 = (C_1-C_4) alkyl,

R^2 = H or CH_3

and

R^3 = 

in which

R^4 = (C_6-C_{75}) aromatic compound,
(C_6-C_{75}) cycloalkyl or
(C_6-C_{75}) alkyl and

where the aromatic compound, cycloalkyl and alkyl are based on diglycidyl compounds.

4. Dispersion according to claim 3, characterised in that in formula (I):

a = 15-20,

R^1 = methyl,

R^2 = H

and

R^3 = $-CH_2-\underset{OH}{CH}-CH_2-O-R^4-O-CH_2-\underset{OH}{CH}-CH_2-$

in which R_4 = $-(C_6H_4)-C_3H_6-(C_6H_4)-$.

5. Use of the emulsifier according to any one of claims 1-4 in the preparation of radiation-curable systems.

6. Use of the emulsifier according to formula (I) in the preparation of radiation-curable systems.

7. Use of a dispersion according to any one of claims 1-4 in the preparation of coatings.

8. Coating based on a dispersion according to any one of claims 1-4.

9. Entirely or partly coated substrate, characterised in that the substrate is coated with a coating according to claim 8.

INTERNATIONAL SEARCH REPORT

Inter aal Application No
PCT/NL 94/00113

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D175/16 C08G18/67

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 507 053 (HUELS) 7 October 1992 see page 3, line 3 - page 5, line 33; claims 1,5	1,2
X	EP,A,0 381 862 (BAYER) 16 August 1990 see page 2, line 50 - page 4, line 37	1
A	DATABASE WPI Week 8816, Derwent Publications Ltd., London, GB; AN 107705 'EMULSIFIER FOR AQUEOUS RESIN DISPERSING BODY' & JP,A,63 054 930 (DAIICHI KOGYO) 9 March 1988 see abstract	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 1994	05. 09. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bourgonje, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/NL 94/00113

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 7814, Derwent Publications Ltd., London, GB; AN 26236 'AQUEOUS COATING COMPOSITION FORMING HARD RIGID FILM' & JP,A,53 019 349 (KANSAI PAINT) 22 February 1978 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte[illegible]nal Application No
PCT/NL 94/00113

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0507053	07-10-92	DE-A-	4110821	08-10-92
		JP-A-	5222145	31-08-93
		US-A-	5200463	06-04-93
EP-A-0381862	16-08-90	DE-A-	3900257	12-07-90
		CA-A-	2007097	06-07-90
		JP-A-	2245015	28-09-90
		US-A-	5095066	10-03-92